REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)

2. REPORT DATE
14 March 2002

3. REPORT TYPE AND DATES COVERED
Final Report covering 07/01/98 - 06/30/01

4. TITLE AND SUBTITLE
Light Control in Fractal Nanoparticles

5. FUNDING NUMBERS
DAAG55-98-1-0425

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
37287.3-PH-H

11. SUPPLEMENTARY NOTES
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12 a. DISTRIBUTION / AVAILABILITY STATEMENT
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13. ABSTRACT (Maximum 200 words)
This final report details the findings of the cited ARO Grant. During the Grant, a number of experiments were performed illustrating the unique characteristics of fractal and fractal/microcavity media, in particular, their capability to support nonlinear optical effecs under conditions of extremely weak incident light. These findings are supported by a number of research papers and conference presentations discussed in the report.

14. SUBJECT TERMS
Laser, Nonlinear, Materials

15. NUMBER OF PAGES
4 (+Memo of Trans)

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
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REPORT TITLE: "Light Control in Fractual Nanoparticles"

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Sincerely, Robert L. Armstrong

(Robert L. Armstrong)

I. Introduction

The control of light beams propagating either in free space or within an optical system is a matter of continuing concern and interest in the scientific and engineering community. Intense, monochromatic, highly directional laser radiation is used in a variety of applications and the control of the phase, amplitude, polarization, and direction of this radiation is of great importance to many optical applications. Both dynamic and passive schemes have been developed to control beam parameters. Dynamic control is generally achieved by means of an active feedback mechanism whereas passive schemes rely on intrinsic, generally nonlinear, properties of materials to achieve the control function.

Recent research has focused on the development of passive optical control devices [1]. Passive systems may be very simple and very fast; however, they place great emphasis on the nonlinear optical properties of the media used to fabricate the control device. Practically any nonlinear process is a potential candidate for such a device since all exhibit a dependence on the intensity or fluence of the incident radiation. The nonlinear process itself can result in absorption, scattering, or refraction of the beam, thereby altering the amount of light incident on the sensitive optical element.

It is natural to inquire whether materials may be fabricated possessing greatly enhanced nonlinearities, typically expressed in terms of exceptionally large values of the third-order nonlinear susceptibility, $\chi^{(3)}$. In this Grant, we have investigated the optical nonlinearities of a novel material, metal colloid fractal aggregates, as well as composites in which the fractal material is embedded in a dielectric microcavity. Since the fractal aggregate exhibits a broadband spectrum of high-Q resonances as does the dielectric microcavity, not only will optical nonlinearities may exceptionally large but they may be excited by modest pump beams.

There are well-established techniques which may be used to fabricate fractal media and to prepare them for experimental study. We have produced fractal aggregates of silver colloidal particles of the order of 20-30 nm in size from a silver sol generated by reducing silver nitrate with sodium borohydride. For experiments in which fractal aggregates are coupled to a dielectric microcavity, we use the simple technique of dipping a hollow microcylinder into a parent solution of aggregates where capillary refill introduces the aggregates into the hollow microcylinder.

II. Work done under grant

The publications (1-13) and conference presentations (a-l) listed in **Section III** describe work done at least partially in support of this grant. During the grant, several types of theoretical and experimental investigations were performed with the unifying goal of understanding and quantifying the enormous enhancement of nonlinear optical responses in fractal aggregate and fractal/microcavity composite media. Some highlights of these investigations are given in the following paragraphs together with literature citations to the entries in **Section III**.

1.Photomodification[1,4,8,b,] ---A well-known physical process in which light can change the stucture of material objects because of absorption. However, in fractal media, the presence of

highly localized, high-Q fractal resonance modes extremely strong spatially localized photomodification in sub-wavelength regions for low pump powers.

2. Near-field[4,8,b]---since the spatial scale of the photomodification is sub-wavelength, near-field microscopy may be exploited in its investigation.

3. Lasing[3,10]---This was the first nonlinear emission from fractal/microcavity composites observed in our laboratory.

4. Hyper-Raman[2,11,12,c,e,]---We have observed 2^{nd} and 3^{rd} order, hyper-Raman scattering (HRS) from molecules adsorbed onto fractal/micricavity composites for pump powers of a few mW.

5. Nonlinear quantum well emission[12,c,d,h]---We have observed nonlinear, multi-photon, emission from metal nanoparticle, quantum well structures using both pulsed an cw pump beams. Nonlinearities occur for extremely low pump powers. We have also observed second harmonic generation (SHG) from these particles, however, with a pump power dependence that varies from the square-law dependence familiar from bulk SHG.

6. Non-degenerate four-wave-mixing (NDFWM)[f,g,i]---We have observed NDFWM from fractal/microcavity composites for mW pumping sources and sub-pW probe beams. We estimate the gain in the NDFWM emission to exceed 10^{12}.

7. Third-order refraction (Kerr effect) and absorption[5,c]---We have observed third-order nonlinearities (refraction and absorption) from metal nanoparticles. These materials exhibit strong optical limiting characteristics.

8. General studies of optical nonlinearities in nanostructured sysrems[6,7,13]---We have observed nonlinearities in nanoscale metal structures and in fractal aggregates of nanoparticles.

III.References

III.A Journal Articles

1."Spectral Dependence of Selective Photomodification in Fractal Aggregates of Colloidal Particles", Physical Review Letters vol 80, p. 1102(1998). (with V. P. Safonov, V. M. Safonov, V. A. Markel, Tu. E. Danilova, N. N. Lepeshkin, W. Kim, and S. G. Rautian)

2."Nonlinear Optical Phenomena in Nanostructured Fractal Materials", Journal of Nonlinear Optical Physics and Materials", vol 7, p. 131 (1998). (with V. Shalaev, and W. Kim)

3."Fractals in Microcavities: Giant, Coupled, Multiplicative Enhancement of Optical Responses", Physical Review Letters, vol 82, p. 4811 (1999). (with W. Kim, V. P. Safonov, and V. M. Shalaev)

4."Near-Field Optical Studies of Local Photomodification in Nanostructured Materials", Journal of Microscopy, vol 194, p. 574 (1999). (with W. Bragg, V. P. Safonov, W. Kim, K. Bannerjee, M. Young, J. Zhu, C. Z. Ying, and V. M. Shalaev)

5."Optical Nonlinearities of Metal-Dielectric Composites", Journal of Nonlinear Optical Physics and Materials, vol8, p. 191 (1999). (with N. Lepeshkin, W. Kim, V. P. Safonov, J. Zhu, C. White, R. Zuhr, and V. Shala

6."Surface Plasmon-Enhanced Radiation Effects in Confined Photonic Systems", Journal of Lightwave Technology, vol 17, p. 2183 (1999). (V. A. Shubin, W. Kim, V. P. Safonov, A. K. Sarychev, and V. M. Shalaev)

7."Percolation and Fractal Composites: Optical Studies', Journal of Nonlinear Physics and Materials, vol 9, p. 105 (2000). (with V. P. Drachev et al)

8."Near-Field Optical Study of Selective Photomodification of Fractal Aggregates", Journal of the Optical Society, vol 18 B, p. 698 (2001). (with W. D. Bragg et al)

9."Large Local Optical Activity in Fractal Aggregates of Nanoparticles", Journal of the Optical Society, vol 18B, p.1896 (2001. (with V. D. Drachev, W. Bragg, V. Podolskiy, V. P. Safonov, W. Kim, C. Ying, and V. M. Shalaev)

10."Low-threshold Lasing and Broadband, Multiphoton Excited Light Emission from Metal Particle-Adsorbate Complexes in a Microcavity", Journal of Modern Optics (in press). (with V. P. Drachev, W. Kim, V. P. Safonov, N. N. Zakovryashin, and V. M. Shalaev)

11. "Broadband, Multiphoton Light Emission from Metal Particle-Adsorbate Complexes in a Microcavity", Journal of the Optical Society (in Press). (with W. Kim, V. Drachev, V. A. Podolskiy, V. P. Safonov, and V. M. Shalaev)

12."Discrete Spectrum of Anti-Stokes Emission from Metal Particles-Adsorbate Complexes in a Microcavity", (Submitted to Physical Review). (with V. Drachev, W. Kim, E. Khallulian, F. Al-Zoubi, V. Podolskiy, V. P. Savonov. and V. M. Shalaev

13. "Fractal Microcavity Composites: Giant Optical Responses", in Optical Properties of Nanostructured Random Media, Springer Topics in Applied Physics, V. Shalaev, ed., 2002. (with W. Kim, V. Drachev, V. Safonov, and V. Shalaev)

III.B Conference Presentations

a."Cubic Nonlinearity of Thin Films with a High Concentration of Gold Nanoparticles Inside a Glass Matrix", SPIE Annual Meeting, Denver, CO, 18-23 July, 1999 (with J. Zhu, V. P. Safonov, N. Lepeshkin, V. M. Shalaev, Z. Ying, C. White, and R. Zuhr)

b."Local Photomodification of Nanomaterials using Near-Field Optics", SPIE Annual Meeting, Denver, CO, 18-23 July, 1999 (with Z. Ying, W. Bragg, K. Bannerjee, J. Zhu, V. P. Safonov, and V. M. Shalaev)

c."High-Power Laser Effects on Milliwatt Lasers", LASERS '99, Quebec, Canada, 13-17 December, 1999. (invited paper) (with R. Montoya, W. Kim, V. P. Safonov, and V. M. Shalaev)

d. "Ultra-Sensitive Chemical and Biological Detection Technology", Joint Conference on Point Chemical and Biological Detection, Williamsburg, VA, 23-27 October, 2000. (with W. Kim, V. P. Drachev, and V. M. Shalaev)

e."Discrete Spectrum of Anti-Stokes Emission from Metal-Adsorbate Complexes in a Microcavity" XVIIth International Conference on Coherent and Nonlinear OpAics, 26 June–1 July, 2001 Minsk, Belarus. (with W. Kim, V. P. Drachev, V. Podolskiy, V. P. Safonov, and V. M. Shalaev)

f."Ultra-Sensitive CB Standoff Detection in Fractal/Microcavity Media", 5th Joint Conference Standoff Chemical and Biological Detection, Williamsburg, VA, 22-24 September, 2001. (with W. Kim)

g."Giant Enhancement of spectral Emissions from Molecules Adsorbed on Silver Fractal/Microcavity Composite Media", Photonics Boston, 28 October-2 November, 2001, Boston, MA (with W. Kim, V. Podolskiy, V. Drachev, V. Safonov, and V. Shalaev)

h."Multi-Photon-Excited Broadband Emission, from Metal Nanoparticles", LASERS'2001, 3-7 December, 2001, Tucson, AZ. (invited paper)

i."Giant Enhancement of Optical Emissions in Fractal/Microcavity Composite Media", Annual Physics of Quantum Electronics Conference, 14-17 January, 2002 (invited paper)(With W. Kim)